ON THE ELECTRIC-QUADRUPOLE TRANSITIONS OF THE OCTAHEDRAL COMPLEXES OF THE TRANSITION METAL IONS

A. S. CHAKRAVARTY

SAHA INSTITUTE OF NUCLEAR PHYSICS, CALCUTTA

(*Received November* 16, 1966; *Resubmitted March* 3, 1967)

ABSTRACT. The algebraic expressions for the oscillator strengths of the electric quadrupole transitions in kd^n octahedral complexes have been derived. The oscillator strength of a particular transition has been shown to be dependent on $\langle r^2 \rangle$ and the energy separation of the two states in which the transition is taking place. A misconception regarding $\langle r^2 \rangle$ has been pointed out, though fortunately it does not effect too much the magnitudes for the oscillator strengths.

INTRODUCTION

In this paper we derive the expressions for the oscillator strengths of the electric quadrupole transitions of $kd^n (k = 3, 4, 5; n = 1, 2, \ldots, 9)$ octahedral complexes. It is well-known that the oscillator strength of an electric quadrupole transition is of the order of 10^{-9} and therefore much too small compared to that of electric-dipole ($f \approx 10^{-3}$ to 10^{-4}) and magnetic dipole ($f \approx 10^{-5}$ to 10^{-6}) transitions. But it may become important in those cases where the electric dipole or magnetic-dipole transitions vanish or are abnormally low. We have also derived the algebraic expressions for the oscillator strengths of electric and magnetic dipole transitions which will be published, shortly. The $\langle r^2 \rangle$ have been calculated using (a) hydrogenic, (b) Slater, (c) Richardson-Watson's wave functions. There is a misconception regarding such calculations for the crystalline complexes which has been cleared up. The details of this misconception has been discussed in details in the next chapter.

THEORY

The oscillator strength for the electric quadrupole transition is given by (Griffith, 1961)

$$f = \frac{2\pi^2 \nu c}{5mh} \sum_{i,j} |\langle a | \vec{r_i}\vec{p_j} + \vec{r_j}\vec{p_i} | b \rangle|^2 \qquad (1)$$

where i and j are the three components of the vectors. Eqn. (1) can be reduced to the standard form by using the relation

$$(E_a - E_b) \langle a | \vec{r_j} | b \rangle = \frac{1}{m} \langle a | (-i\hbar \vec{p_j}) | b \rangle \qquad (2)$$

Eqn. (2) is valid provided the eigen functions a and b are the exact solutions of the Schrodinger's equation and therefore strictly valid for a single electron in a central force field (the hydrogen atom problem). Using Eqn. (2), we get

$$<a|\vec{r_i}\vec{p_j}+\vec{r_j}\vec{p_i}|b> = -2\pi im\nu_{ab}<a|\vec{r_i}\vec{r_j} - \tfrac{1}{3}r^2\delta_{ij}|b>$$

$$= -2\pi im\nu_{ab}<a|\vec{N_{ij}}|b> \quad .. \quad (3)$$

where $\vec{N_{ij}}$ is the quadrupole tensor and ν is the energy difference in cm^{-1} between the ground and the excited state under consideration. The quadrupole tensor $\vec{N_{ij}}$ for a single electron has for its components xy, yz, zx and x^2-y^2, $z^2-1/3r^2$. In octahedral symmetry O_h, (xy, yz, zx) form a basis for t_{2g} and $(x^2-y^2, z^2-1/3r^2)$ form a basis for e_g. The quadrupole tensor for n electrons, therefore, has off-diagonal elements which form a basis for T_{2g} and diagonal elements forming a basis for E_g. It can be easily shown that the diagonal elements vanish between the ground term and all the excited terms. We are therefore left with only T_{2g}. Thus our Eqn. (3) can be written as,

$$<a|\vec{r_i}\vec{p_j}+\vec{r_j}\vec{p_i}|b> = -2\pi im\nu_{ab}<a|r_i r_j|b> \quad .. \quad (4)$$

The Hamiltonian for Eqn. (2) is given by

$$H=\sum_{k=1}^{n}\left(\frac{1}{2m}p_k^2-\frac{Ze^2}{r_k}\right)+\sum_{k<\lambda}^{n}\frac{e^2}{r_{k\lambda}} \quad .. \quad (5)$$

where p_k is the momentum vector of the k-th electron and r_k its distance from the nucleus, m the mass of the electron, $-e$ its charge, $+Ze$ the charge on the nucleus and $r_{k\lambda}$ the distance from the k-th to the λ-th electron. It is important to note that in the above Hamiltonian there is no term representing the potential energy for the crystalline electric field of a particular symmetry.

We now test the equivalence of both sides of Eqn. (4) by using the different types of wave functions i.e., the hydrogenic, Slater's or Hartree-Fock self consistent wave functions. We, however, notice in Eqn. (4) that the R.H.S. is always non-vanishing for crystalline complexes. When an ion enters into a crystalline complex with the ligands (negatively charged dipoles) surrounding it in a particular symmetry then there will be splitting of the energy levels of the ion due to the electrostatic interaction of the crystal field produced by the ligands (Bethe, 1929). For example, when $Ti^{3+}(3d^1)$ forms an octahedral complex, the $3d$-state of the ion splits up into E_g (doublet) and T_{2g} (Triplet). The mean energy separation of E_g and T_{2g} is written as $10\,Dq$. This is our ν_{ab} in Eqn. (4) which is always non-zero for crystalline complexes. The matrix element $<a|r_i r_j|b>$ is also non-zero because this is nothing but $<\bar{r^2}>$ over the states a and b. Thus the R.H.S. of

Eqn. (4) is non-vanishing irrespective of the form of the wave functions chosen. Now, the matrix element on the L.H.S. of Eqn. (4) can be shown to be

$$\frac{2\hbar}{i}\left(-\frac{1}{7\sqrt{3}}\right)\left[\int_0^\infty u(r)u'(r)dr+2\int_0^\infty ru(r)\ \frac{\partial u'(r)}{dr}\ dr\right] \tag{6}$$

after performing the angular integration with the wave functions

$$a(E_g \text{ type}) = \frac{u(r)}{\quad}\ Y_2^0$$

$$b(T_{2g} \text{ type}) = \frac{u'(r)}{r}\left[\frac{1}{i\sqrt{2}}(Y_2^2 - Y_2^{-2})\right] \tag{7}$$

where $u(r) = rR(r)$ and $u'(r) = rR'(r)$

and the radial and angular wave functions are already normalized separately.

The reason for writing the two different radial functions for E_g and T_{2g} is that the E_g and T_{2g} wave functions interact differently with the cubic field (Watson, 1960). If, however, we assume the same radial function for both a and b (which is the usual practice), then $3d$ shell is spherical and will not interact with the cubic field. This can be easily verified by integrating the integral in Eqn. (6) by parts assuming $u(r) = u'(r)$, whence the third bracketed expression in Eqn. (6) is identically zero and this is true for all the three types of wave-functions (i.e., hydrogenic, Slater's and H-F wave functions). This means that the L.H.S. of Eqn. (4) goes to zero when the R.H.S. remains non-vanishing always. Thus it is proved that Eqn. (4) does no longer hold good for the crystalline compleses. The physical reason of such inequivalence can be understood from the following arguments. The above mentioned wave functions are true for an atom or ion but when this atom or ion forms a crystalline complex with the ligands then these wave functions are bound to be distorted due to the crystalline electric field created by the neighbouring ligands or in other words, the radial distribution of the electrons of the central ion gets somewhat altered and in any accurate calculation of the properties of such crystalline complexes we must use the accurate wave functions if they are available.

One method of constructing such wave functions would obviously be to start with the hydrogen atom problem after including in the total Hamiltonian a term containing the potential energy due to the crystal field and then try to solve the differential equation for the radial distribution which will now have different solution because of the crystal potential we have included. An analytical solution even for a single electron (the many electron solution would be enormously difficult to obtain) would be difficult to get but the numerical solution can be

obtained with the help of an electronic computer. In one case such wave fuctions have been obtained by Watson (1960) and this is for $Mn^{2+}(3d^5)$ in cubic field. In this case he has shown that the radial wave functions for E_g and T_{2g} would be different and he has found a very close agreement with experiment in his calculation for 10Dq, including the sign of Dq (Kleiner, 1952). The wave functio are

$$U_{3z^2-r^2}(r) = p_{12}N_{12}r^3 \exp(-Z_{12}r)+p_{13}N_{13}r^3 \exp(-E_{13}r)$$
$$+p_{14}N_{14}r^3 \exp(-Z_{14}r)+p_{15}N_{15}r^3 \exp(-Z_{15}r) \quad \ldots (8)$$
$$u'_{xy}(r) = p'_{12}N_{12}r^3 \exp(-Z_{12}r)+p'_{13}N_{13}r^3 \exp(-Z_{12}r)$$
$$+p'_{14}N_{14}r^3 \exp(-Z_{14}r)+p'_{15}N_{15}r^3 \exp(-Z_{15}r)$$

The magnitudes of p_{12}, N_{12}, Z_{12}, p'_{12} etc. are given in his paper (Watson, 1960) and we do not mention them here.

Using the above functions we have calculated both the sides of Eqn. (3) and find that the non-vanishing equivalence of Eqn. (4) is fully maintained.

Hence before calculating the oscillator strengths of the electric quadrupole transitions we must remember that we are using the correct crystal field wave functions in which case only we can proceed to calculate the R.H.S. of Eqn. (4). The matrix element $<\overline{r^2}>$ on the right hand side of Eqn. (4) does not vary too much (within 2%) whether we use the free ion wave functions or the cubic field wave functions. The following Table I gives the magnitudes of the radial part of the matrix element in atomic units for the different type of wave functions chosen :

TABLE I

Type of wave function	$<a\|\, r_i\, r_j\,\|\, b>$ in A.U.
1. Hydrogenic or Slater	4.01780
2. Hartree-Fock	1 54803
3. Watson's Cubic Field	1.53955

It is evident from Table I that if we calculate the oscillator strengths using Hydrogenic or Slater's wave functions then the calculated values of the oscillator strengths would be about five times larger than those calculated with Hartree-Fock or Watson's cubic field wave functions.

Inserting Eqn. (4) in Eqn. (1), we get,

$$f = \frac{8\pi^4 m\nu^3 c}{5h} \sum_{i,j} |a|\, \eta_{ij}\, |b>|^2 \qquad (9)$$

where η is the psendo-vector (yz, zx, xy).

Using Slater's determinantal wave functions and in the strong field approximation, the n electron matrix element is reduced ultimately to that of a single electron. The oscillator strength is then calculated in the usual way from Eqn. (9), where we use the following integrals :

$$\langle yz|\eta|z^2\rangle = \frac{1}{7\sqrt{3}}\langle\bar{r^2}\rangle_{kd} \qquad \langle zx|\eta|x^2-y^2\rangle = \frac{1}{7}\langle\bar{r^2}\rangle_{kd}$$

$$\langle yz|\eta|x^2-y^2\rangle = -\frac{1}{7}\langle\bar{r^2}\rangle_{kd} \qquad \langle xy|\eta|z^2\rangle = -\frac{2}{7\sqrt{3}}\langle\bar{r^2}\rangle_{kd}$$

$$\langle zx|\eta|z^2\rangle = \frac{1}{7\sqrt{3}}\langle\bar{r^2}\rangle_{kd} \qquad \langle xy|\eta|x^2-y^2\rangle = 0$$

where

$$\langle\bar{r^2}\rangle_{kd} = \int_0^\infty R^2_{kd}(r)r^4dr \qquad (K = 3, 4, 5) \qquad \ldots (10)$$

In Tables IIA, IIB and IIC, we have presented the values of $\langle\bar{r^2}\rangle_{kd}$ for $k = 3$ 4, 5 for different values of E_{eff} in the approximations (a) and (b) calculated $\langle\bar{r^2}\rangle_{kd}$ also in the approximation (c), since the SCF wave functions of Richardson *et al.* (Richardson 1962, 1963) are available only for $3d^n$ ions. The Table III gives the algebraic expressions for the oscillator strengths of the electric quadrupole transitions for the different configurations $kd^n (k = 3, 4, 5; n = 1$ through $9)$. For a particular value of k and n and for a particular complex, the oscillator strength for a particular transition can be immediately obtained from Eqn. (9) by inserting the proper values for ν, the energy difference in cm^{-1} and $\langle\bar{r^2}\rangle_{kd}$ from the Tables IIA, IIB and IIC into Table III. Lastly in Table IV we present a few magnitudes of the oscillator strengths of the electric quadrupole transitions for aquo complexes of the $3d^n$ transition metal ions. The experimental energy separation, ν, between which the transition is taking place has been obtained mostly from Ballhausen (1962) and Jorgensen (1954, 1955) and also from current literatures. In our calculations we have taken $\langle\bar{r^2}\rangle_{3d}$ from Table IIA obtained by using Richardson *et al.* wave functions.

From Table IV it is evident that the oscillator strengths are very small compared to those of the electric dipole ($f \sim 10^{-3}-10^{-4}$) and magnetic dipole ($f \sim 10^{-5}-10^{-6}$) transitions. Since there is no experimental data available on these transitions at the present we cannot compare our theoretical values.

TABLE IIA

Variation of $\langle r^2 \rangle_{3d}$ with E_{eff} using Hydrogenic or Slater and Richardson *et al.* wave function.

	Z_{eff}	$\langle \bar{r}^2 \rangle_{3d}$ using hydrogenic or Slater wave function	Ions	$\langle \bar{r}^2 \rangle_{3d}$ using wave function of Richardson *et al*
1.	3.5	2.880534×10^{-16}	Ti^{3+}	0.239096×10^{-16}
2.	4.0	2.205409×10^{-16}	V^{3+}	0.212284×10^{-16}
3.	5.0	1.411462×10^{-16}	V^{2+}	0.240972×10^{-16}
4.	6.5	0.835184×10^{-16}	Cr^{3+}	0.191940×10^{-16}
5.	7.5	0.627316×10^{-16}	Cr^{2+}	0.21480×10^{-16}
6.	8.5	0.488395×10^{-16}	Mn^{3+}	0.173456×10^{-16}
7.	9.5	0.390986×10^{-16}	Mn^{2+}	0.192286×10^{-16}
			Fe^{3+}	0.157285×10^{-16}
			Fe^{2+}	0.173982×10^{-16}
			Co^{3+}	0.143282×10^{-16}
			Co^{+2}	0.156598×10^{-16}
			Ni^{2+}	0.142880×10^{-16}
			Cu^{2+}	0.120423×10^{-16}

TABLE IIB

$\langle r^2 \rangle_{4d}$ Using Hydrogenic and Slater Wavefunctions with Varying Z_{eff}

Z_{eff}	$\langle \bar{r}^2 \rangle_{4d}$ Using Hydrogenic w.f.	$\langle \bar{r}^2 \rangle_{4d}$ Using Slater w.f.
4.0	8.821638×10^{-16}	4.730088×10^{-16}
5.0	5.645848×10^{-16}	3.027256×10^{-16}
6.0	3.920728×10^{-n6}	2.102261×10^{-16}
7.0	2.880534×10^{-n6}	1.544518×10^{-16}
8.0	2.205409×10^{-16}	1.182522×10^{-16}
9.0	1.742545×10^{-16}	0.934338×10^{-16}
10.0	1.411462×10^{-n6}	0.756814×10^{-16}
12.0	0.980182×10^{-16}	0.525565×10^{-16}

TABLE IIC

$\langle r^2 \rangle_{5d}$ Using Hydrogenic and Slater Wavefunctions with Varying Z_{eff}

Z_{eff}	$\langle \bar{r}^2 \rangle_{5d}$ Using Hydrogenic w.f.	$\langle \bar{r}^2 \rangle_{5d}$ Using Slater w.f.
4.0	$23.629387 \times 10^{-16}$	6.301170×10^{-16}
5.0	$15.122808 \times 10^{-16}$	4.032748×10^{-16}
6.0	$10.501950 \times 10^{-16}$	2.800520×10^{-16}
7.0	7.715718×10^{-16}	2.057524×10^{-16}
8.0	5.907346×10^{-16}	1.575292×10^{-16}
9.0	4.667533×10^{-16}	1.244675×10^{-16}
10.0	3.780702×10^{-16}	1.008187×10^{-16}
12.0	2.625487×10^{-16}	0.700130×10^{-16}

TABLE III

The oscillator strengths of electric-quadrupole transitions of octahedral kd^n compleses

Configuration	Transition ($g \rightarrow g$) (Ground State → Excited St)	The Oscilator Strength f (Eqn. 9)
kd^1	$^2T_2 \rightarrow {}^2E$	$\frac{32}{735}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$
kd^2	$^3T_1 \rightarrow {}^3T_1$	$\frac{16}{245}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$
	$\rightarrow {}^3T_2$	$\frac{16}{735}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$
kd^3	$^4A_2 \rightarrow {}^4T_1\{t_{2g}^2(^3T_1)e_g\}$	$\frac{32}{245}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$
kd^4	$^3T_1 \rightarrow {}^3A_2\{t_{2g}^3(^2E)e_g\}$	$\frac{32}{2205}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$
	$\rightarrow {}^3E^{(1)}\{t_{2g}^3(^4A_2).e_g$	$\frac{32}{2205}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$
	$\rightarrow {}^3E^{(2)}\{t_{2g}^3(^2E).e_g\}$	$\frac{32}{2205}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$
	$\rightarrow {}^3T_1{}^{(1)}\{t_{2g}^3(^2T_1).e_g\}$	$\frac{8}{735}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$
	$\rightarrow {}^3T_1{}^{(2)}\{t_{2g}^3(^2T_2).e_g\}$	$\frac{8}{245}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$
	$\rightarrow {}^3T_2{}^{(1)}\{t_{2g}^3(^2T_0)e_g\}$	$\frac{8}{245}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$
	$\rightarrow {}^3T_2{}^{(2)}\{t_{2g}^3(^2T_2).e_g\}$	$\frac{8}{735}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$
$^5E\{t_{2g}^3(^4A_2).e\}$	$\rightarrow {}^5T_2\{t_{2g}^2(^3T_1)e_g^2(^3A_2)\}$	$\frac{16}{245}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$
kd^5	$^2T_2 \rightarrow {}^2A_1\{t_{2g}^4(^1E)e_g\}$	$\frac{32}{2205}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$
	$\rightarrow {}^2E^{(1)}\{t_{2g}^4(^1A_1)e_g\}$	$\frac{32}{2205}\frac{\pi^4 m\nu^3 c}{h}\langle r^2\rangle^2_{kd}$

TABLE III (Continued)

Configuration	Transition ($g \rightarrow g$) (Ground State - Excited St)	The Oscillator Strength f(Eqn. 9)
	$\rightarrow {}^2E^{(2)}\{t_{2g}^4({}^1A_1)e_g\}$	$\frac{32}{2205}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{kd}$
	$\rightarrow {}^2T_1^{(1)}\{t_{2g}^4({}^3T_1)e_g\}$	$\frac{8}{245}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{kd}$
	$\rightarrow {}^2T_1^{(2)}\{t_{2g}^4({}^1T_2)e_g\}$	$\frac{8}{245}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{kd}$
	$\rightarrow {}^2T_2^{(1)}\{t_{2g}^4({}^3T_1)e_g\}$	$\frac{8}{245}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{kd}$
	$\rightarrow {}^2T_2^{(2)}\{t_{2g}^4({}^1T_2)e_g\}$	$\frac{8}{245}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{kd}$
kd^8	${}^1A_1 \rightarrow {}^1T_2\{t_{2g}^5({}^2T_2)e_g\}$	$\frac{64}{245}\pi^4 m\nu^3 c\ \langle\overline{r^2}\rangle^2$
	${}^5T_2\{t_{2g}^4({}^3T_1)e_g^2({}^3A_2)\}$	
	$\rightarrow {}^5E\{t_2^3({}^4A_2)e_g^3({}^2E)\}$	$\frac{32}{735}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{k}$
kd^7	${}^2E \rightarrow {}^2T_1^{(1)}\{t_{2g}^5({}^2T_2)e_g^2({}^1E)\}$	$\frac{8}{245}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{kd}$
	$\rightarrow {}^2T_1^{(2)}\{t_{2g}^5({}^2T_2)e_g^2({}^3A_2)\}$	$\frac{8}{245}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{kd}$
	$\rightarrow {}^2T_2^{(1)}\{t_{2g}^5({}^2T_2)e_g^2({}^1E)\}$	$\frac{8}{245}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{kd}$
	$\rightarrow {}^2T_2^{(2)}\{t_{2g}^5({}^2T_2)e_g^2({}^1A_1)\}$	$\frac{8}{245}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{kd}$
kd^7	${}^4T_1\{t_{2g}^5({}^2T_2)e_g^2({}^3A_2)\}$	
	$\rightarrow {}^4T_2\{t_{2g}^4({}^3T_1)e_g^3({}^2E)\}$	$\frac{16}{735}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{kd}$
	$\rightarrow {}^4T_1\{t_{2g}^4({}^3T_1)e_g^3({}^2E)\}$	$\frac{16}{245}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{kd}$
kd^8	${}^3A_2 \rightarrow {}^3T_1\{t_{2g}^5({}^2T_2)e_g^3({}^2E)\}$	$\frac{32}{245}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{kd}$
kd^9	${}^2E \rightarrow {}^2T_2$	$\frac{16}{245}\frac{\pi^4 m\nu^3 c}{h}\langle\overline{r^2}\rangle^2_{kd}$

TABLE IV

The electric quadrupole oscillator strengths for the $3d^n$ transition metal ion aquo complexes

Configuration	5Ion	Complex	Transition ($g \rightarrow g$)	Energy difference (cm^{-1})	$f \times 10^9$
$3d^1$	Ti^{3+}	$Ti(H_2O)_6^{3+}$	$^2T_2 \rightarrow {}^2E$	20,300	0.0835
$3d^2$	V^{3+}	$V(H_2O)_6^{3+}$	$^3T_1 \rightarrow {}^3T_1$	25,200	0.1890
			$\rightarrow {}^3T_2$	17,100	0.0196
$3d^3$	Cr^{3+}	$Cr(H_2O)_6^{3+}$	$^4A_2 \rightarrow {}^4T_1$	24,500	0.0284
$3d^6$	Fe^{2+}	$Fe(H_2O)_6^{2+}$	$^5T_2 \rightarrow {}^5E$	10,400	0.0059
$3d^7$	Co^{2+}	$Co(H_2O)_6^{2+}$	$^4T_1 \rightarrow {}^4T_2$	8,200	0.0011
			$\rightarrow {}^4T_1$	20,000	0.0514
$3d^8$	Ni^{2+}	$Ni(H_2O)_6^{2+}$	$^3A_2 \rightarrow {}^3T_1$	14,700	0.0339
$3d^9$	Cu^{2+}	$Cu(H_2O)_6^{2+}$	$^2E \rightarrow {}^2T_2$	12,600	0.0076

ACKNOWLEDGMENT

The author wishes to express his sincere thanks to Dr. D. K. Ray of this Institute for many helpful discussions and useful comments and suggestions Thanks are also due to Prof. A. K. Saha for his interest in the investigation.

REFERENCES

Ballhausen, C. J., and Jorgensen, C. K., 1955, *Acta Chem. Scand.*, **9**, 397.

Ballhausen, C. J., 1962, *Introduction to Ligand Field Theory*, McGraw-Hill Book Company, Inc., New York.

Bethe, H. A., 1929, *Ann. Phys.*, **133**, 760.

Griffith, J. S., 1961, *The Theory of Transition Metal Ions*, Cambridge University Press

Kleiner, W. H., 1952, *J. Chem. Phys.* **20**, 1784.

Richardson, J. W., Nieuwpoort, W. C., Powell, R. R. and Edgell, W. F., 1962, *J. Chem. Phys.* **86**, 1057.

Richardson, J. W., Powell, R. R., and Nieuwpoort, W. C., 1963, *J. Chem. Phy*, **38**, 796.

Watson, R. E., 1960, *Phys. Rev.*, **117**, 742.